



National Institute of Standards & Technology

Certificate

Standard Reference Material[®] 1921a

Infrared Transmission Wavelength Standard

This Standard Reference Material (SRM) is intended primarily for use in calibrating the wavelength (wavenumber) scale of spectrophotometers in the infrared (IR) spectral region from 3.2 μm to 18.5 μm (540 cm^{-1} to 3125 cm^{-1}). SRM 1921a is a matte finish polystyrene film approximately 38 μm thick with a 25 mm diameter exposed area, centered 38 mm from the bottom of a cardboard holder, which is 5 cm \times 11 cm \times 0.2 cm in size.

Certified Wavelength (Wavenumber) Values: The spectral transmittance of a statistically representative group of the polystyrene film SRM specimens was measured under both vacuum and purge conditions. The positions of absorption bands in the range of 3.2 μm to 18.5 μm were obtained using both a centroid method as well as a band minimum determination method. Thirteen of the band locations were selected for certification based on experimental and statistical analysis results. The certified wavelength values and associated uncertainties of these bands are shown in Tables 1 and 3 for the centroid and band minimum methods, respectively. The corresponding wavenumber values and associated uncertainties of the bands are shown in Tables 2 and 4, respectively. See section entitled “Band Wavenumber and Wavelength Determination” for details. To aid the user in distinguishing among the bands during measurement, a spectrum is shown in Figure 1, with arrows identifying the certified bands. For band wavelength and wavenumber values measured in air or under purge conditions, see section entitled “Correction for Air/Nitrogen Purge”.

The expanded uncertainty, U , is provided for each certified band wavelength and wavenumber. It is the product of the coverage factor, $k = 4$, and the combined standard uncertainty. The combined standard uncertainty is the root sum of squares of all the uncertainty components [1-3].

NOTICE AND WARNING TO USERS

Expiration of Certification: The certification of this SRM is valid until **31 December 2010**, provided the SRM is stored and handled in accordance with the “Storage and Handling and Instructions for Use” sections of this certificate. However, certification will be nullified if the SRM is damaged, contaminated, or exposed to excess humidity.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Storage and Handling: When not in use, SRM 1921a should be kept in its accompanying protective cover. For storage, it is advisable to keep the SRM in a desiccator cabinet. The SRM should always be handled with care; the exposed film surface should never be touched by fingers or any other objects. Dust may be removed by blowing with clean, dry air.

The overall direction and coordination of the technical measurements leading to certification were performed under the supervision of R.V. Datla and L.M. Hanssen of the NIST Optical Technology Division.

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Optical Technology Division

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The technical measurements leading to certification were performed by C. Zhu and L.M. Hanssen of the NIST Optical Technology Division.

Statistical consultation was provided by J.J. Filliben of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Measurement Conditions: The calibration measurements were made using a Bomem DA-3.02¹ Fourier transform spectrophotometer. The instrument room temperature was maintained at 22 °C ± 1 °C and the humidity ranged from 30 % to 50 % during the measurements. Calibration measurements were made under vacuum level pressures of 50 Pa (0.4 Torr), as well as under a purge gas of clean air (with CO₂ and H₂O removed). Details of the measurement methodology can be found in reference 3.

Source of Material: The polystyrene film used for SRM 1921a was taken from a single roll. It was manufactured by the Dow Chemical Company and donated by the Coblenz Society.¹

INSTRUCTIONS FOR USE

Calibration Measurements: Prior to calibration with SRM 1921a, the spectrophotometer should be set up under the following conditions:

- Step 1. Set the instrumental resolution to any value up to 2 cm⁻¹. A resolution of 4 cm⁻¹ can be used with Fourier transform spectrophotometers provided that Boxcar or no apodization is used in the Fourier transform processing [4,5]. Within these constraints the most appropriate resolution for calibration is the one that is used for typical sample measurements.
- Step 2. Set the source aperture to provide sufficient signal for measurement, yet not greater than that required to maintain measurement resolution. The setting should not be so large that the wavenumber shift error becomes significant [6] or the detector becomes significantly non-linear [7,8].
- Step 3. Close and purge or evacuate the sample chamber for a time suitable for the instrument to reach pressure and temperature equilibrium.
- Step 4. Obtain at least six transmittance spectra of SRM 1921a for statistical evaluation.
- Step 5. Analyze the resulting spectra for band locations as described in the next section
- Step 6. When appropriate, apply the results to correct the spectrometers wavelength/wavenumber scale as described in the last section.

Steps 3 to 5 should be repeated in sequence at least six times. The resulting transmittance spectra should be analyzed for band locations as described below.

Band Wavenumber and Wavelength Determination: Two methods have been used to obtain calibrated band locations: a centroid method with band fraction of 0.5 and a band minimum determination method. Both methods have been applied to spectra in wavenumbers. Wavelength values can be obtained from the wavenumber values through the relationship $\lambda\nu = 1$, where λ is the wavelength in cm. The user can select either Tables 1 and 2 if they apply the centroid (with band fraction of 0.5) method, or Tables 3 and 4 if they apply any method designed to obtain the band minimum.

Centroid Method

The original method used to determine the band wavenumber (ν) and wavelength (λ) values of SRM 1921a is the centroid (also known as the center of gravity) method [9,10]. This procedure is performed on the transmittance spectra using wavenumber values only. The wavenumber value is defined as the number of waves per unit length (cm). Refer to Figure 2 when using the following band determination procedure.

¹Certain commercial equipment, instrumentation, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

First, the bounds of an initial wavenumber range (ν_{\min} to ν_{\max}) enclosing the band are determined; they are the wavenumber values at which transmittance relative maxima occur on either side of the band. Next, the differences between the transmittance values at each bound and the transmittance at the band minimum,

$$\Delta T(\nu_{\max}) = [T(\nu_{\max}) - T(\nu_{\text{band min}})] \text{ and } \Delta T(\nu_{\min}) = [T(\nu_{\min}) - T(\nu_{\text{band min}})],$$

are determined. Then half the value of the smaller of $\Delta T(\nu_{\max})$ and $\Delta T(\nu_{\min})$, $\Delta T_0/2$ is determined. The wavenumber range (ν_1 to ν_2) to be used in the centroid calculation is that between the wavenumber values where the transmittance values on either side of the band equal the minimum transmittance value plus $\Delta T_0/2$,

$$\nu_{1,2} = \nu, \text{ where } T = T_{1/2} \equiv T(\nu_{\text{bandmin}}) + \Delta T_0 / 2$$

The specific data end points of the spectrum, $h = \nu_1$ and $k = \nu_2$ are selected so that $T_h \geq T_{1/2} > T_{h+1}$ and $T_k < T_{1/2} < T_{k-1}$ for adjacent points. The centroid equation for finite sums (below) effectively averages data at the ends, ν_1 and ν_2 , to reduce the error due to the finite data spacing. The formula used is

$$\nu_{\text{Cen}} = \nu_k + \Delta \nu \left\{ \frac{\sum_{i=h-1}^k (i-k + \frac{1}{2}) \left[\frac{(T_i + T_{i+1})}{2} - T_{1/2} \right]}{\sum_{i=h-1}^k \left[\frac{(T_i + T_{i+1})}{2} - T_{1/2} \right]} \right\}$$

where $\Delta \nu$ is the frequency spacing.

Band Minimum Determination Method

A recently developed method was designed and applied to accurately determine the band minimum (or maximum) value to obtain calibration values for SRM 1921a. This method is called the *extrapolated centroid method* [11,12]. It entails the calculation of centroid values for a set of fractions (approaching zero fraction) of the band and extrapolating a curve fit through the set of values to a value for zero fraction that corresponds to the band minimum (or maximum). Results of any method designed to find the band minimum should produce essentially the same result and hence be directly comparable [5,13].

Correction for Air/Nitrogen Purge: The NIST certification measurements were performed in vacuum. Hence, the wavelength values reported in Table 1 are vacuum values where the index of refraction, n , equals 1. For instruments that operate under vacuum, calibration measurements of SRM 1921a can be directly compared to values in Table 1. Also, for instruments which give vacuum wavenumber and wavelength values (such as Fourier transform infrared (FTIR) spectrometers which use helium-neon lasers for determination of the wavenumber scale) even when operated under air or purge gas, no corrections are necessary.

In all other cases when measurements of SRM 1921a are made under air, nitrogen, or other purge gas, the wavenumber and wavelength values need to be adjusted for the index of refraction of the gas ($n = 1.00026$ for dry nitrogen gas at atmospheric pressure and $T = 298 \text{ K}$) [14,15]. Thus, for nitrogen purge, the measured wavenumber values should be divided by 1.00026, and the wavelength values should be multiplied by 1.00026 to compare to the certified values in Table 1.

Corrections to Instrument Wavenumber Scale: The resulting N ($N \geq 6$) values for each peak at wavenumber, ν , should be averaged to obtain a single *band wavenumber value* (laboratory mean, \bar{y}_ν), and the standard deviation of the values, s_ν , should be calculated. In order to determine whether or not the laboratory measurements are biased relative to SRM 1921a, calculate the difference, δ_ν , between the laboratory mean, \bar{y}_ν , and the certified value, C_ν , as follows:

$$\delta_\nu = \bar{y}_\nu - C_\nu$$

A practical limit for evaluating consistency with the certified value is:

$$\delta_c = (t_{N-1} 0.95) s_v / \sqrt{N} + U$$

where $t_{N-1} 0.95$ is the critical value from the student's distribution with $N - 1$ degrees of freedom for a two-sided 95 % confidence interval [16] and U [1,2] is the uncertainty from Table 2. For example, if $N = 6$, then $t_5 0.95 = 2.571$. If $\delta_v > |\delta_c|$, then the difference is greater than can be explained by chance, and the wavenumber scale of the instrument should be corrected to the SRM. If this is the case, generally a linear least squares fit of δ_v to ν for the 13 peaks should provide a sufficient correction to the spectrophotometer scale. However, if $\delta_v \leq |\delta_c|$, the wavenumber scale of the spectrophotometer is considered to be accurate and correction is not advised.

Table 1. Certified Band Centroid Wavelength Values (in Vacuum)

Band Wavelength (μm)	Expanded Uncertainty, U (μm)
18.3618	0.1119
11.8752	0.0172
11.0272	0.0012
9.7244	0.0019
9.3528	0.0073
8.6609	0.0006
6.3168	0.0007
6.2447	0.0003
3.50860	0.00009
3.33177	0.00011
3.30428	0.00008
3.26794	0.00007
3.24450	0.00008

Table 2. Certified Band Centroid Wavenumber Values (in Vacuum)

Band Wavenumber (cm^{-1})	Expanded Uncertainty, U (cm^{-1})
544.61	3.32
842.09	1.22
906.85	0.10
1028.34	0.21
1069.20	0.84
1154.62	0.08
1583.07	0.18
1601.37	0.08
2850.14	0.07
3001.41	0.10
3026.38	0.07
3060.03	0.06
3082.14	0.08

Table 3. Certified Band Minimum Wavelength Values (in Vacuum)

Band Wavelength (μm)	Expanded Uncertainty, U (μm)
18.5182	0.0596
11.8797	0.0090
11.0291	0.0030
9.7256	0.0044
9.3543	0.0105
8.6617	0.0009
6.3170	0.0008
6.2449	0.0003
3.50946	0.00011
3.33194	0.00033
3.30477	0.00020
3.26794	0.00019
3.24438	0.00023

Table 4. Certified Band Minimum Wavenumber Values (in Vacuum)

Band Wavenumber (cm^{-1})	Expanded Uncertainty, U (cm^{-1})
540.01	1.74
841.77	0.64
906.69	0.24
1028.21	0.47
1069.03	1.20
1154.51	0.11
1583.03	0.19
1601.31	0.06
2849.44	0.09
3001.25	0.30
3025.93	0.18
3060.03	0.18
3082.25	0.22

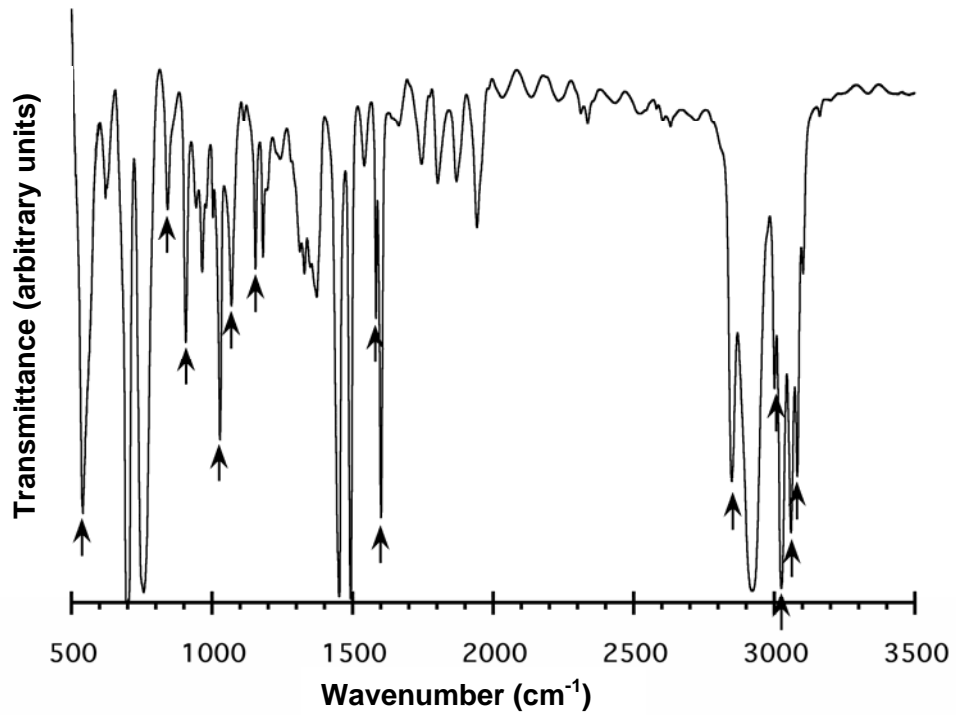


Figure 1. Spectrum of polystyrene film showing locations of certified absorption bands

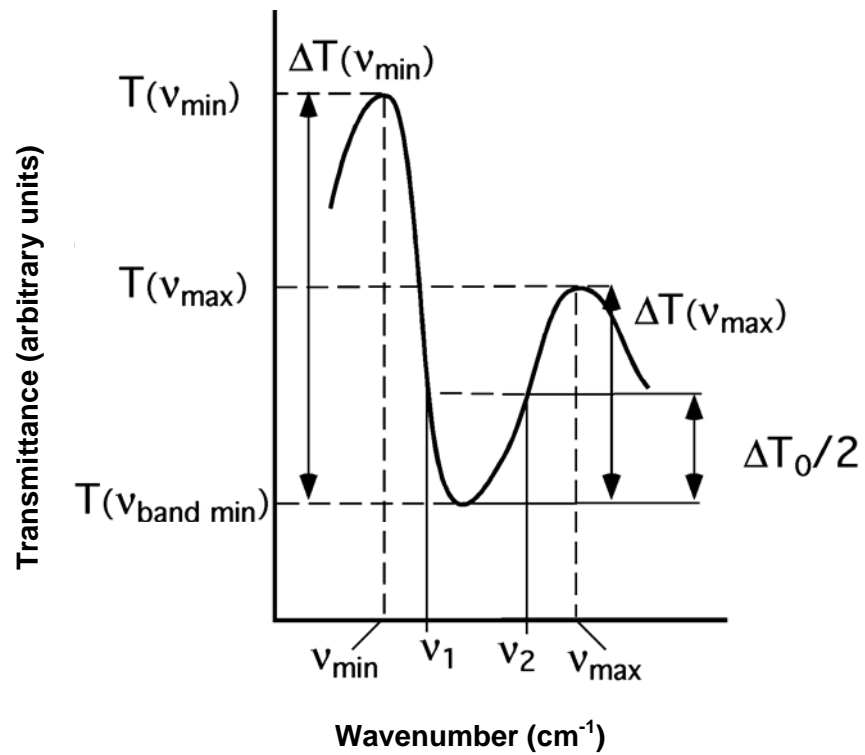


Figure 2. Diagram indicating parameters used in the band wavenumber determination method (see text for details)

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Certificate Revision History: 09 November 2006 (Update of expiration date and editorial changes); 15 June 2004 (This revision adds a date for NIST Spec. Publ. 260-122); 19 December 2002 (Update of expiration date and additional certification values, measurement information, and instructions for use); 24 March 1998 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet <http://www.nist.gov/srm>.